염료 태양전지용 투명 전도성 박막제작 및 특성 고찰

(Fabrication of transparent conductive oxides
for Dye-sensitized solar cell application)

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Abstract

Titanium-doped indium oxide (ITiO) films were prepared on soda-lime glass substrate using a magnetic null discharge (MND) sputter source. The ITiO thin films containing 10 wt.% Ti showed the minimum resistivity of $\rho=5.5\times10^{-3}\Omega$-cm. The optical transmittance increases from 70% at 450 nm to 80% at 700 nm in visible spectrum. Photoelectron peaks for In 3d, Ti 2p, O 1s and C1s were detected for the ITiO film in the binding energy range of 0 to 1100 eV. The surface roughness of the sample showed a change from 10 nm to 50 nm. The ITiO film used for TCO layer of DSCs exhibited an energy conversion efficiency of about 3.8 % at light intensity of 100 mW/cm^2.

1. Introduction

The recent advances in photovoltaic (PV) technology [1] have triggered considerable interests in the fields of solar power as an alternative and renewable source of electricity. Also, solar cells now allow applications for various electronic equipment, including satellites, calculators, remote radiotelephones, and advertising signs. The dye-sensitized solar cells (DSCs) devised by Prof. M.Grätzel in 1991[1, 2] has been characterized by its electrochemical cell structure through the use of iodine solution, and not silicon semiconductors. Due to its low cost and low burden on the environment, it has gathered attention and hope worldwide as the next generation in solar cells [3, 4]. Typically, DSCs consist of a transparent conducting oxide (TCO) layer and dye sensitized TiO_2 electrode in contact with electrolyte and is completed by an inert counter electrode. Transparent conducting oxide (TCO) is an important part in the construction of DSCs because of its low sheet resistance, the sufficient light transparent ability and the high photoelectrical response as a porous photo-electrode material of DSCs. The TCO materials most commonly used for DSCs are F-doped tin-oxide (FTO) and indium-tin-oxide (ITO). The FTO/ITO films can be mainly prepared by the chemical vapor deposition (CVD) method. However, the CVD process is costly and somewhat complicate for the application of mass production. Also, the FTO/ITO films have limitations in their infrared ray (IR) transmission and thermal resistance as a transparent conductor. Thus, more studies are still required to enhance these defects. The potential advantage of a titanium-doped indium oxide (ITiO) relative to the FTO/ITO of comparable sheet resistance resides in its high mobility and near-IR transmittance [4]. The properties of ITiO layer show that the long-wavelength fall off in transmittance does not occur until 1500nm compared to about 1000nm for an 8 W/sq. Usually, DSCs are still responsive in the 1000-1100nm range, and thus benefit from improved TCO layer transmission in this near-IR wavelength range. In this work, The MND sputter source realizes the uniform processing as well as the successful reduction of plasma localization from the wall effect by controlling the position and the diameter of the MN region. And various electrical, optical properties and surface structure the films were measured by the 4-point probe, XPS and atomic force microscopy (AFM), respectively. Finally, the photovoltaic performance of the prepared DSCs made by the ITiO film was evaluated.

2. Experimental

2.1 Preparation of ITiO films

Figure 1(a) and 1(b) shows the target of the MND sputter source with the magnetic field formed by the permanent magnets and the calculated magnetic field line distribution on the target surface, respectively. The system consisted of 8 pairs of permanent magnets arranged circularly. The array of magnets formed eight null regions perpendicular to the ITiO target surface. The target was in doughnut shape 70 mm in width. The distance between the target and a substrate was 200 mm. Cooling water was circulated through the target to prevent overheating. The ring-typed outer magnetic holder could be rotated at intervals of 5o during deposition for controlling the MN field dynamically. By the rotation of the MN field, the enhancement of target erosion and film uniformity were possible. As shown in Fig. 1(b) with the arrangement of permanent magnet (of 120 mT), the resulting magnetic field is in a sector of 90° (from 0°~90°). With the same magnet strength of any 4 adjacent groups of magnets arranged as shown in the figure, the MN region is formed as a point at the center of the plane containing the magnets; spatially a line in the z-direction. The MN points are formed at (64.3 mm, 22.5°) and (64.3 mm, 67.5°) from the target surface in the z direction; the B=0 line can be seen formed. The r_N (=64.3 mm) is the target radial including the null points. When the high frequency electric field is applied to the null field region via the target by a 13.56 MHz rf generator, electrons move in the electric and magnetic fields. From the calculation results involving the energy of electrons, the mean energy around the MN region was found to be more than twice as much compared with other regions by the effective electron heating [5-8]. Therefore, in the application of MND sputter source, controlling the position and the diameter of the MN region can be easily achieved, which realizes the uniform processing as well as the successful reduction of plasma localization from the wall effect. This is the unique feature of the MND sputter source. The process conditions for the ITiO film preparation can be briefly summarized as shown in Table 1. At first, the chamber was exhausted vacuum to 2×10^{-6} Torr or less. The working gas of Ar(95%) and O_2(5%) was introduced to the chamber, and the total pressure was maintained at 5 mTorr during deposition. The RF power (P_{rf}) of 500 W was supplied to a sintered ITiO target (90 wt.% In_2O_3 and 10 wt.% TiO_2). The distance between the target and a soda-lime glass substrate with sectional area of 25×40 mm was 150 mm. During deposition, pure Ar/O_2(5%) gas was introduced into the chamber, by adjusting Ar/O_2 inlet to maintain an Ar/O_2(5%) pressure of 5 mTorr for ITiO film preparation. These deposition conditions provided growth rates of about 10nm/min. After the film deposition, the Ar/O_2(5%) pressure was kept constant, until the temperature holder decreased to room temperature. Post-annealing in vacuum was performed at 300℃ for 3 consecutives hours. This step is necessary to promote the formation of best ITiO film. The deposited ITiO films were taken out of the chamber to confirm the properties the films.

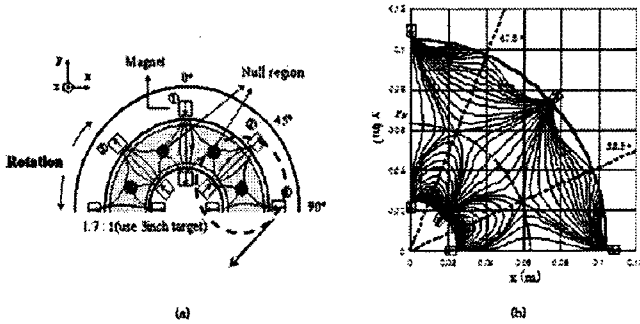


Fig. 1. Schematic arrangement of the experimental apparatus
(a) Front view of MND sputter source
(b) Calculated magnetic field line distribution.

RF power	500W
Working pressure	5mTorr
Operating gas(Partial pressure)	Ar-O_2 (5%)
Target-substrate distance(d_s)	150mm
Deposition time	60 min.
Annealing temperature	300℃

Table. 1. Summary of the ITiO film depositions

2.2 Preparation of DSCs and Evaluation

The prepared ITiO/TiO_2 films were dye-sensitized by soaking the films for 24 - 48 h at 25℃ in a dye solution i.e., 0.3 mM solution of cis-di(thiocyanate)bis (2,2'-bipyridyl-4,4'-di-carboxylate) ruthenium(II) (R535, N3 dye) in ethanol. Fig. 2 shows an image of the prepared DSCs sample. Pt counter electrodes were prepared on ITO coated glass substrates. A few droplets of platinum solution consisting of 5 mM $PtCl_4$ in isopropanol were spread on the substrate and heated at 450℃ for 30 min in air. The solar cells were assembled by placing the dye-sensitized ITiO/TiO_2 electrode and the Pt counter electrode together in a sandwich structure using 60 μm thick Surlyns film (DuPont) as spacer and edge sealant. Adherence of the Surlyn film to the substrates was induced by pressing the substrates together on a heating plate at 110℃. This reduced the film thickness to about 40 μm. The electrolyte solution was composed of 0.1 M LiI, 0.1 M I_2, 0.5 M 1,2-dimethyl-3-propylimidazolium iodine and 0.5 M tert-butylpridine in methoxypropionitrile. The channels were hence sealed with Torr seals vacuum sealant. The short-circuit photpcurrent (J_{sc}) and the open-circuit voltage (V_{oc}) were measured using a solar simulator (Yamashita Denso YSH-80).

3. Results and discussion

Fig. 3 shows the resistivity of the ITiO films prepared by MND sputter source with/without annealing as a parameter of the film thickness. The resistivity decreased with increasing film thickness for both case. In case annealing at 300°C, the resistivity became constant at $1.4\times10^{-3}\Omega$-cm for thickness of 100 nm, while resistivity of the film without annealing became constant at $6.1\times10^{-3}\Omega$-cm at same thickness.

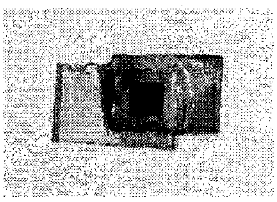


Fig. 2. Image of the prepared DSCs sample (glass size: 1.25cm×2cm)

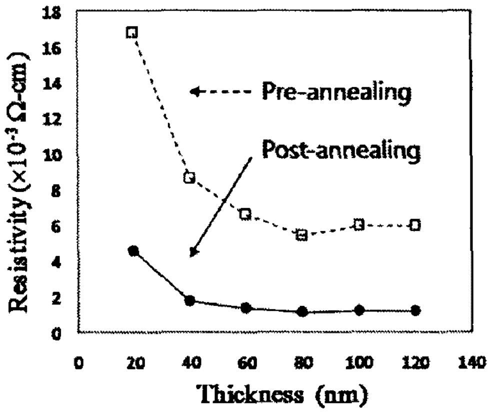


Fig. 3. Dependence of the resistivity of the ITiO films on the thickness

Fig. 4 shows the optical transmittance spectrum of ITiO thin films (100nm) deposited on glass with/without annealing. Information concerning optical transmittance is important in evaluating the optical performance of TCO films. A high transparency for the ITiO thin film is required in applications with TCO electrode for optoelectronic devices. As shown in this figure, the transparency increases from 70% at 450 nm to 80% at 700 nm which is sufficiently high for use as a TCO electrode. The UV absorption edge is located at approximately 350 nm. The annealing process leads to the films with a steeper optical absorption curve, which indicates a better crystallinity of the films and lower defect density near the band edge. The increase in optical transmittance with temperature can be attributed to the increase of structural homogeneity and crystallinity [10].

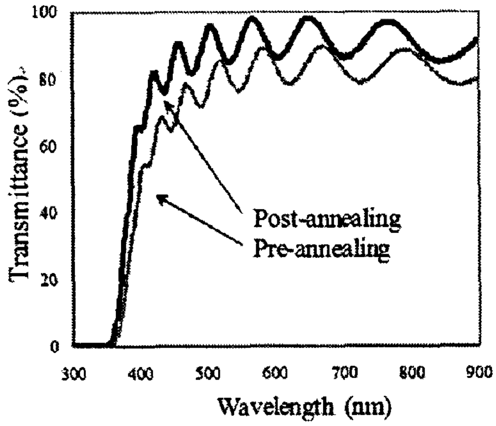
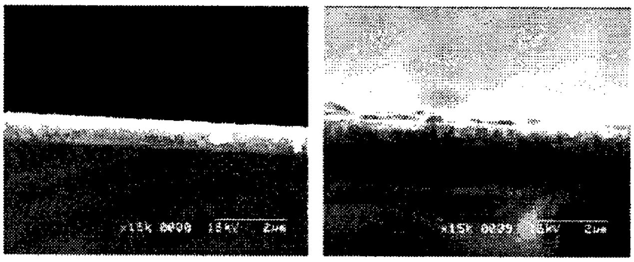


Fig. 4. Optical transmittance spectra for the ITiO films with/without annealing

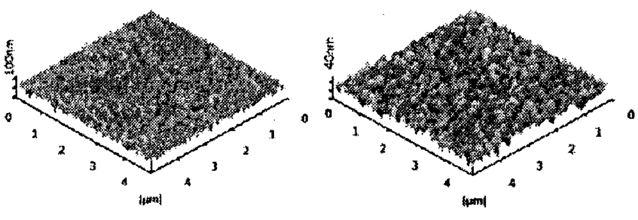
Fig. 5 shows the cross-sectional SEM images of the prepared ITiO films with/without annealing. Although, we can not found a clear distinction between two SEM images, both SEM images depict that the crevice of the ITiO sample near the cutting edge of the substrate shows neither defects nor voids along the interface of the film surfaces. This indicates that the MND sputtering method can prepare ITiO films with dense and uniform properties. This can be confirmed from the dense and columnar microstructure observed by AFM and XPS spectra as shown in Figs. 6 and 7, respectively.



(a) (b)

Fig. 5. Cross-sectional SEM images on the surface of the prepared ITiO films with/without annealing
(a) with annealing (b) without annealing

The AFM measurement confirmed the annealing effect on the ITiO films shown in Fig. 6. After annealing, the surface roughness of the sample showed a change from 10 nm to 50 nm. This can be explained by the fact that the heat treatment promotes the crystal nucleation of the films. One can conclude that more crystalline ITiO films can grow on the glass substrate by an appropriate post-heat treatment.



(a) (b)

Fig. 6. AFM images of the ITiO films with/without annealing
(a) with annealing (b) without annealing

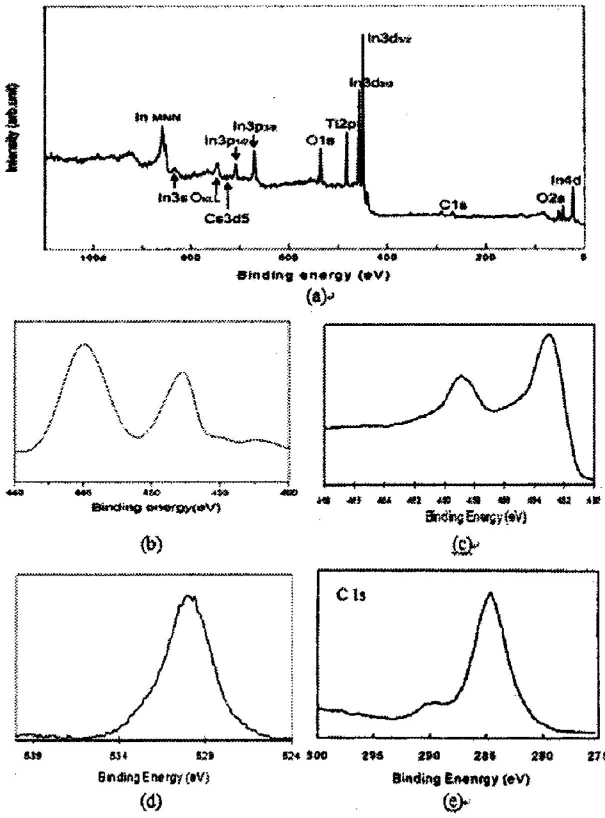


Fig. 7. XPS spectra of the ITiO film
(a) wide spectra (b) In 3d spectra (c) TiO_2 spectra (d) O1s spectra (e) C1s spectra

XPS measurements were carried out to evaluate the Cs concentration in the ITiO thin film prepared by MND sputter source. Photoelectron peaks for In 3d, Ti 2p, O 1s and C1s were detected for the ITiO film in the binding energy range of 0 to 1100 eV as shown in Fig. 7. The binding energy of the O 1s photoelectron peak is at 530 eV. A C 1s peak at a binding energy of 284 eV is also observed on the surface of the film. The presence of this peak is related to the surface pollution which corresponds to the fact that the samples were exposed to air before the XPS measurements. The XPS spectra for O 1s peak, In 3d and Ti 2p are shown in Figs. 7b-7e respectively. Figs. 7b-7e indicate that oxygen is bonded to the indium and Ti and that ITiO is formed. The binding energy of In 3d at 445.1 eV measured from ITO film shown in Fig. 7b can be attributed to the In^{3+} bonding state from In_2O_3[11]. The binding energy of Ti 2p is at 487. 1 eV as shown in Fig.7c and corresponds to the Ti^{+} bonding state from TiO_2.

Finally, the prepared DSC was irradiated with a Light Drive 1000 lamp through an unfrared-blocking filter. The current-voltage characteristics were recorded by varying an external potential compensating the photo-voltage. The integral photocurrent (short-circuit current) was obtained without the external potential. The photoelectric efficiency was calculated with respect to the solar spectra through a calibration of the Light Drive 1000 lamp with direct sunlight. The overall efficiency η of a photovoltaic cell can be calculated from the expression:

$$\eta = \frac{J_{SC} V_{OC} FF}{P_S}$$

where J_{sc} is the integral photocurrent density (current obtained at the short-circuit condition, divided by the area of the cell), V_{oc} is the open-circuit voltage, FF is the fillfactor (related to the series resistance for a practical solar cell), and P_s is the intensity of the incident light. Fig.8 illustrates the current-voltage-power characteristics of the prepared DSC. It exhibited an energy conversion efficiency of 3.8% at 100mW/cm^2 light intensity. Considering a maximum conversion efficiency of ~7.2% for a conventionally prepared nanocrystalline solar cell [12], it is probable that our technique is feasible and effective.

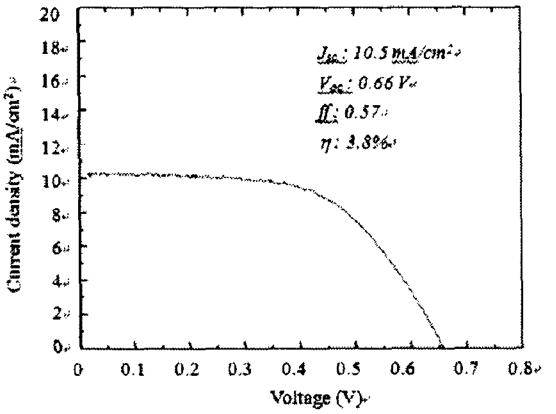


Fig. 8. I-VcharacteristicsofaDSCbasedonITiO/TiO2films

4. Conclusion

In this work, titanium-doped indium oxide (ITiO) films were prepared on soda-lime glass substrate using a magnetic null discharge (MND) sputter source. The electrical and optical properties of the transparent conductive ITiO film and the photovoltaic performance of the prepared DSCs were examined. The ITiO thin films containing 10 wt.% Ti showed the minimum resistivity of ρ=5.5×10^{-3}Ω-cm. The optical transmittance increases from 70% at 450 nm to 80% at 700 nm in visible spectrum. In addition, XPS and AFM measurements were performed to investigate the surface structural properties of the films. Finally, the ITiO film used for TCO layer of dye-sensitized solar cells(DSCs) exhibited an energy conversion efficiency of about 3.8% at light intensity of 100 mW/cm^2. It can be therefore seen that the ITiO films obtained by MND sputter system exhibited good transparent conductive properties, well suited for DSCs application.

Acknowledgments

This research was financially supported by the Ministry of Education, Science Technology (MEST) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation. And Mr. J.H Hu and J. H. Kim were partly supported financially from the Brain Busan 21 program.

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